Kinetic Study on Palladium Dichloride-catalyzed Carbomethoxylation of Styrene under Compressed Carbon Monoxide in a Redox System (Commemoration Issue Dedicated to Professor Yoshimasa Takezaki on the Occasion of his Retirement)

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Kinetic Study on Palladium Dichloride-catalyzed Carbomethoxylation of Styrene under Compressed Carbon Monoxide in a Redox System

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Methyl cinnamate and dimethyl phenylsuccinate were synthesized in good yields by carbomethoxylation of styrene with carbon monoxide and methanol in a redox system of palladium dichloride-benzoquinone. The effects of concentrations of styrene, catalyst, benzoquinone and methanol, carbon monoxide pressure and temperature, upon their rates were kinetically investigated. The rate equation derived on the basis of the proposed mechanism, has been able to explain the experimental results.

KEY WORDS: Carbomethoxylation/ Carbon monoxide reaction/ Methyl cinnamate/ Dimethyl phenylsuccinate

1. INTRODUCTION

The interesting syntheses of β-alkoxy ester, α, β-unsaturated monoester and saturated diester from olefin and carbon monoxide in the presence of $PdCl_2$ and the oxidant such as $CuCl_2$ and/or O_2, have been reported by Fenton[1] and Stille,[2] shown as

$$RCH=CH_2 \xrightarrow[\text{"Pd"}]{CO,\ R'OH} RCH(OR')CH_2CO_2R' + RCH=CHCO_2R' + RCH(CO_2R')CH_2CO_2R'.$$

Stille has proposed the mechanism involving the acidity-controlled formation of an intermediate [(CO) Pd(olefin)] and a carboalkoxy palladium intermediate [($R'O_2C$) Pd (olefin)] as the key steps; the lower acidity of the medium was supposed to favor the formation of carboalkoxy palladium intermediate which might not lead to β-alkoxy ester as $RCH(OR')CH_2CO_2R'$ but to mono- and/or di-ester.

However, there has been so far reported no kinetic study on this type of carbonylation in the palladium-redox system.

So, we carried out the kinetic investigation to elucidate the mechanism in more detail, employing styrene as olefin, methanol as alcohol, *p*-benzoquinone as the oxidant of the reduced palladium, and benzonitrile as solvent: the title reaction is expressed as

$$PhCH=CH_2 + CO + MeOH + \frac{1}{2}PdCl_2 \longrightarrow PhCH=CH(CO_2Me) + HCl + \frac{1}{2}Pd,$$

$$PhCH=CH_2 + 2CO + 2MeOH + PdCl_2 \longrightarrow PhCH(CO_2Me)CH_2(CO_2Me) + 2HCl + Pd,$$

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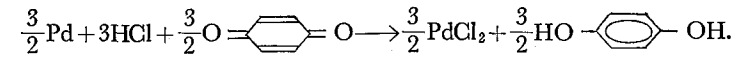


p-Benzoquinone, instead of $CuCl_2$, was employed by reason of its high solubility in solvent to let the reaction proceed in a homogeneous system.

2. EXPERIMENTAL

Material.

Palladium(II) dichloride, *p*-benzoquinone and hexamethyl benzene were commercially purchased and used without further purification. Methanol was used after dried by molecular sieve 3A. Styrene and benzonitrile were distilled before use.

Carbon monoxide was prepared by decomposing formic acid in hot sulfuric acid and its purity was above 98%.

Dichloro *bis*-benzonitrile palladium(II) was prepared by the conventional method.[3]

Procedure.

Reactions were carried out in a glass-tube placed in a stainless-steel autoclave (*ca.* 280 *ml*) equipped with a Teflon sampling line and a Teflon stirrer.

The desired amounts of catalyst, *p*-benzoquinone, styrene, methanol, benzonitrile and hexamethylbenzene were charged in the autoclave, which was then purged with nitrogen.

The autoclave was heated up to the desired temperature and then maintained at that tempereture. Immediately after carbon monoxide had been introduced up to the desired pressure, stirring (1000~2000 *rpm*) was started and this time was marked as zero time. At a certain interval of time, a sample (*ca.* 1 *ml*) was withdrawn through the sampling line into a trap chilled in an ice bath within 1 min. In order to keep the pressure constant, carbon monoxide was supplied from a reservoir from time to time.

Analysis of product.

The products were identified by comparison of their retention time in the gas chromatography with those of authentic samples.

An Apiezon-greese column (2 *m*) with a nitrogen carrier-gas was used at 160°C for the determination of amounts of methyl cinnamate, dimethyl phenylsuccinate and styrene with hexamethylbezene as the internal standard.

3. RESULTS

3.1. Preliminary Survey

In order to know the outline and favorable conditions for the carbonylation of styrene (ST), preliminary experiments ware carried out and results are given in Table I, from which the follwings have been found out.

The desired methyl cinnamate (MC) and dimethyl phenylsuccinate (DS) were formed smoothly and the material balance of the charged ST was almost satisfying.

Table I. Preliminary experiments

Exp. No.	Reaction conditions							Results			
	ST (*mmol*)	MeOH (*ml*)	$PdCl_2$ (*mmol*)	Q (*mmol*)	P_{CO} (kg/cm^2)	T (°C)	time (*min*)	ST (*mol%*)	MC (*mol%*)	DS (*mol%*)	DS/(DS+MC) (*mol%*)
1	7.98	2	0.352	15.4	2	105	60	45.1	46.4	8.00	14.7
2	8.03	1	0.350	25.4	2	105	60	58.0	26.4	5.85	18.1
3	8.00	1	0.213	25.4	2	130	60	-	44.9	0.88	1.92
4	8.02	1	0.209	25.4	20	105	60	39.0	6.61	50.1	88.4
5	8.04	1	0.348	15.5	20	120	120	48.3	1.74	46.1	96.4
6	0	2.5	0.209	15.4	20	105	120	$(COOMe)_2$ 3 mol% based on MeOH			
C1	3.82	4.2	0.42	15.5	1	75	15	-	4.8	2.9	62.3
C2	3.78	4.2	0.40*	15.5	1	75	15	-	5.0	3.0	62.5

* $PdCl_2(PhCN)_2$ was used as catalyst. Solvent: benzonitrile (100 *ml*). Q: benzoquinone. Recovered amount of ST, yields of MC and DS are based on the charged amount of ST.

Effects of $PdCl_2$ and $PdCl_2(PhCN)_2$ on the initial rate were examined, since PhCN was employed as solvent in this reaction and $PdCl_2(PhCN)_2$ is known to be formed by the reaction of $PdCl_2$ with PhCN.[3]

No different effect on the rate was observed between them as shown in runs of No. C1 and No. C2. Therefore, $PdCl_2$ was used as the starting catalyst in the subsequent experiments.

It should be noted that carbon monoxide pressure and temperature are the major factors to control the selectivity for the desired ester formation; increased pressure of carbon monoxide and lowered temperature enhance the selective formation of DS, while

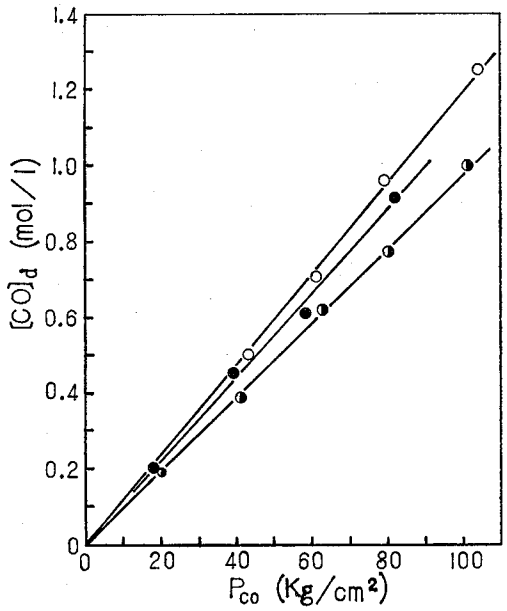
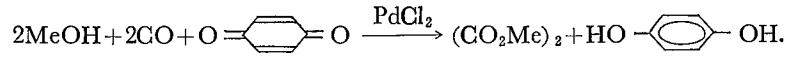


Fig. 1. Solubility of carbon monoxide in benzonitrile
○ 75°C, ● 90°C, ◑ 105°C

lowered pressure and raised temperature enhance the selective formation of MC.

From the result of the blank experiment (No. 6) made without ST under the same conditions as in No. 4, it turned out that methy oxalate was never produced in more than trace quantities.

So, its formation reaction shown as below, can be ignored in this title reaction.



Besides, methoxylated products such as PhCH=CH(OMe) and PhCH(OMe)CH_2-CO_2Me were not detected in the gas chromatography, and this suggested no formation of methoxy palladium intermediate such as [(MeO)Pd(PhCH=CH_2)Cl_2] in the reaction system employed here.

As the solubility of carbon monoxide in benzonitrile was needed in discussion, its measurements were made and results are given in Fig. 1. Henry's constants obtained from the tangent of the straight line at each temperature, are listed in Table VIII.

3.2. Kinetic Measurements

Kinetic measurements were made in a guide given by the preliminary experiment and the results will be described as below, in three separate cases of the selective formation of DS, the selective formation of MC and the non-selective formations of DS and MC.

Table II. Effects of concentrations of ST and catalyst (105°C, 105 kg/cm^2)

Reaction conditions					Results			
$PdCl_2$ (mol/l)	ST (mol/l)	MeOH (mol/l)	Q (mol/l)	time (min)	yield of DS ($mol\%$)	S_{DS} ($mol\%$)	k_{obs}^{DS} (s^{-1})	A_{obs}^{DS} ($l/mol\cdot s$)
0.00704	0.0805	0.250	0.155	15	19.2	94.1	from Fig. 2, 2.3×10^{-4}	from the dotted line in Fig. 2, 3.3×10^{-2}
				30	33.7	94.4		
				45	45.1	95.6		
				60	57.2	96.6		
				90	65.9	95.6		
				120	80.4	97.6		
0.00349	0.0803	0.250	0.154	15	9.5	94.1	from Fig. 2, 1.1×10^{-4}	
				45	26.0	–		
				60	31.7	93.5		
				90	43.6	94.6		
				120	57.4	96.3		
0.00177	0.0800	0.250	0.155	30	9.0	97.8	from Fig. 2, 5.5×10^{-5}	
				60	18.3	95.8		
				90	24.8	96.9		
				120	33.9	99.1		
				180	43.2	>99		
				240	52.9	>99		

S_{DS} : selectivity of DS.

3.2.1. Selective Formation of DS

The effects of reaction variables upon the rate were examined in case of DS being formed above 90% in the selectivity.

Results examined as to the concentrations of ST and catalyst, are given in Table II and Fig. 2, where the solid lines show the first order plots with respect to the concentra-

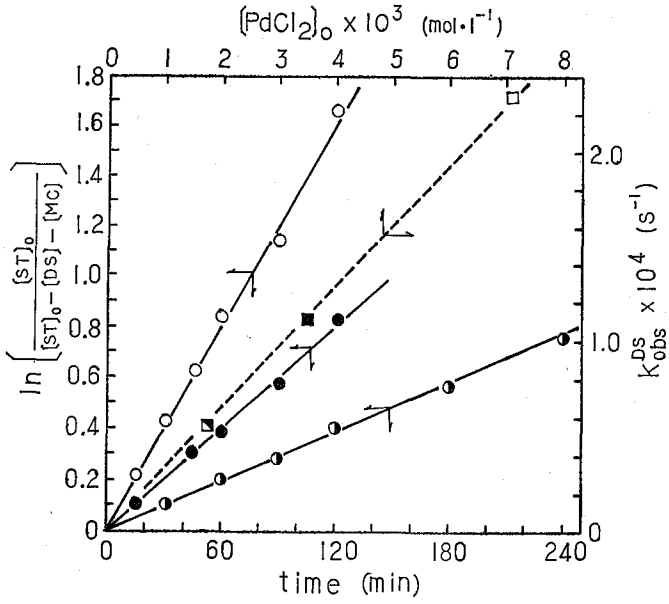


Fig. 2. Effects of ST and catalyst concentrations on DS formation
105°C, 150 *kg/cm*², $[PdCl_2]_0$: ○, □ 7.04×10^{-3} (*mol/l*),
●, ■ 3.49×10^{-3} (*mol/l*), ◑, □ 1.77×10^{-3} (*mol/l*)

tion of ST at each given initial concentration of catalyst. Since the selectivity of DS formation is above 94%, the rate of DS formation, R_{DS}, can be expressed as Eq. (1) in good approximation,

$$-\frac{d[ST]}{dt} \fallingdotseq R_{DS}=k^{DS}_{obs}[ST]. \qquad (1)$$

From a dotted line which showed the plot of k^{DS}_{obs} against the initial concentration of catalyst, the rate was proved to be of the first order with respect to the concentration of catalyst.

Thus, the rate of DS formation is given by Eq. (2),

$$R_{DS}=A^{DS}_{obs}[PdCl_2]_0[ST], \qquad (2)$$

and values of k^{DS}_{obs} and A^{DS}_{obs} are listed in Table II.

Effects of MeOH concentration and *p*-benzoquinone concentration were examined and their results are given in Table III and IV, respectively. The rate or A^{DS}_{obs} was independent of these variables.

Finally, we made the examinations of effects of carbon monoxide pressure and

Table III. Effect of MeOH concentration (105°C, 150 kg/cm^2)

Reaction conditions				Results	
MeOH (mol/l)	$PdCl_2$ (mol/l)	ST (mol/l)	time (min)	DS ($mol\%$)	S_{DS} ($mol\%$)
0.25	0.00704	0.080	30	33.7	94.4
			60	57.2	94.7
			120	80.4	97.6
0.50	0.00700	0.080	30	34.0	-
			60	56.5	96.6
			120	81.0	98.3

Q: 0.155 mol/l. S_{DS}: selectivity of DS.

Table IV. Effect of benzoquinone concentration 105°C, 150 kg/cm^2)

Reaction conditions					Results	
Q (mol/l)	$PdCl_2$ (mol/l)	ST (mol/l)	MeOH (mol/l)	time (min)	DS ($mol\%$)	S_{DS} ($mol\%$)
0.155	0.00704	0.0805	0.25	30	33.7	94.4
				60	57.2	94.7
				120	80.4	97.6
0.278	0.00700	0.0797	0.25	30	32.4	94.1
				60	54.9	94.8
				120	82.0	98.8

Table V. Effects of carbon monoxide pressure and temperature

Reaction conditions							Results	
T (°C)	P_{CO} (kg/cm^2)	ST (mol/l)	$PdCl_2$ (mol/l)	MeOH (mol/l)	Q (mol/l)	S_{DS} ($mol\%$)	$k_{obs}^{DS}\times10^5$ (s^{-1})	$A_{obs}^{DS}\times10^2$ ($l\cdot mol^{-1}\cdot s^{-1}$)
75	10	0.0453	0.00355	0.250	0.153	93	6.0	1.7
	20	0.0804	0.00348	0.250	0.153	93	4.2	1.2
	29	0.0801	0.00501	0.250	0.154	93	5.0	0.9
90	20	0.0796	0.00353	0.250	0.156	92	12	3.5
	30	0.0802	0.00349	0.250	0.153	93	9.4	2.7
	40	0.0800	0.00350	0.250	0.155	94	8.8	2.3
105	35	0.0800	0.00209	1.00	0.155	90	19	9.1
	75	0.0803	0.00356	0.250	0.155	91	20	5.6
	100	0.0803	0.00571	0.250	0.154	94	26	4.6
	150	0.0805	000.704	0.250	0.154	94	23	3.3

temperature on the rate or A_{obs}^{DS}, and obtained results as given in Table V.

A_{obs}^{DS} has been found to be the complicated function of the pressure of carbon monoxide. It should be noted especially that increase in pressure caused the depression of the rate.

3.2.2. Selective Formation of MC

In expectation of the selective formation of MC, the attempts were made under the lower pressure than in the preliminary experiment.

As shown in Figs. 3 and 4, this expectation was realized. In Fig. 3, open circles

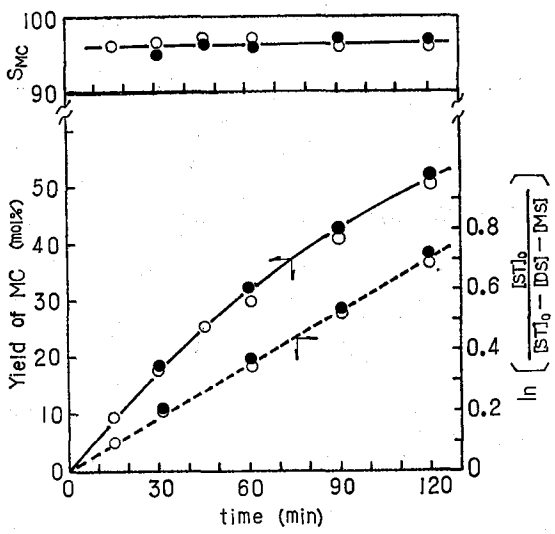


Fig. 3. Time-dependence of MC yield and effect of ST concentration
120°C, 1 *kg/cm²*, $[PdCl_2]_0$ 6.82×10^{-4} *mol/l*, MeOH 1.25 *mol/l*, Q 0.155 *mol/l*. S_{MC}; selectivity of MC
$[ST]_0$; initial concentration of ST, ○ 0.0384 *mol/l*, ● 0.0194 *mol/l*

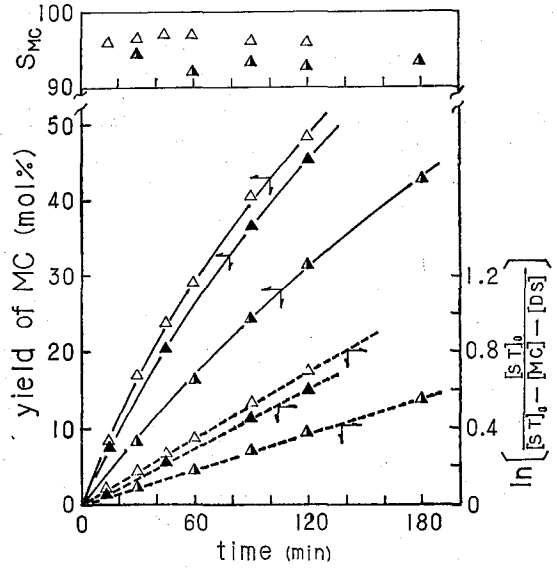


Fig. 4. Effect of catalyst concentration
120°C, 1 *kg/cm²* $[ST]_0$ 0.0384 *mol/l*, MeOH 1.25 *mol/l*, Q 0.155 *mol/l*, $[PdCl_2]_0$ (initial concentration of catalyst in *mol/l*); △ 6.82×10^{-4}, ▲ 5.69×10^{-4}, ○ 3.44×10^{-4} S_{MC} (see Fig. 3)

show the results at 0.038 *mol/l* of ST concentration and closed circles show those at 0.019 *mol/l*.

Both were coincident within the experimental error as seen in the time-dependence of yields (solid lines) and in the plot of ln[ST] *vs.* time (dotted line).

k_{obs}^{MC}'s obtained from the dotted lines, were plotted against the initial concentration of catalyst to give the straight line through origin, as shown in Fig. 5.

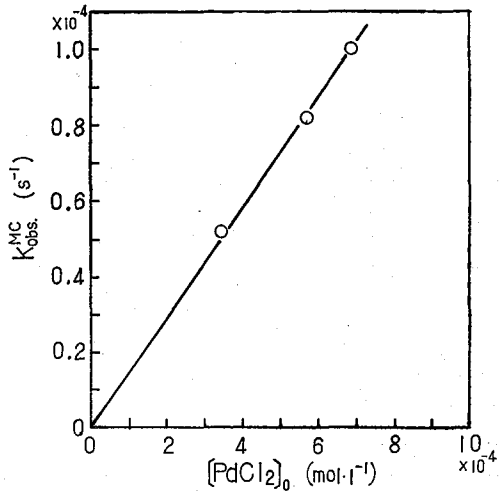


Fig. 5. Relationship between k_{obs}^{MC} and $[PdCl_2]_0$
120°C, 1 *kg/cm²*

Hence, the rete of MC formation, R_{MC}, can be expressed by Eq. (3),

$$R_{MC}=k_{obs}^{MC}[ST]=A_{obs}^{MC}[ST][PdCl_2]_0. \quad (3)$$

Besides, the rate was also found to be independent of both concentration of MeOH and benzoquinone, as in case of the selective formation of DS.

3.2.3. Non-selective Formations of both MC and DS

Both MC and DS were formed in fair yields under the conditions: $75°C \leqq T \leqq 105°C$ and $1\ kg/cm^2 \leqq P_{co} \leqq 15\ kg/cm^2$.

Some typical examples are given in Table VI. k_{obs}'s were calculated by Eq. (4) to satisfy the first rate law with regard to the concentration of ST at the given condition.

$$R=k_{obs}[ST], \quad (4)$$

where $R=-d[ST]/dt=d([MC]+[DS])/dt$.

The produced mole ratio of DS to MC ($\equiv Z$) was found to be constant through the whole reaction period at each fixed condition.

Since A_{obs} is equal to $k_{obs}/[PdCl_2]_0$, A_{obs} is expressed as,

$$A_{obs}=A_{obs}^{MC}+A_{obs}^{DS}. \quad (5)$$

The produced mole ratio of DS to MC is given by Eq. (6),

Table VI. Examples of time-dependence of MC and DS formations

Ex.	Reaction time (*min*)	Yield (*mol%*) MC	DS	$Z_{obs} \equiv$DS/MC (mole ratio)	$k_{obs} \times 10^5$ (1/*s*)	$A_{obs}^{MC} \times 10^2$ (*l/mol·s*)	$A_{obs}^{DS} \times 10^3$ (*l/mol·s*)
	30	9.3	5.6	0.58	9.0	1.4	7.9
	60	17.3	10.7	0.59	9.1	1.4	8.0
A	90	24.2	14.9	0.62	9.2	1.4	8.4
	120	30.2	17.2	0.60	8.9	1.3	7.9
				av. 0.60	av. 9.1	av. 1.4	av. 8.1
	15	3.5	5.9	1.7	11	1.2	2.0
	30	6.5	10.6	1.6	10	1.1	1.7
	45	9.6	16.0	1.7	11	1.2	2.0
B	60	11.6	18.7	1.6	10	1.1	1.7
	90	15.5	26.1	1.7	10	1.0	1.8
	120	18.5	32.5	1.8	9.9	1.0	1.8
	150	20.8	38.2	1.8	9.9	1.0	1.8
				av. 1.7	av. 10	av. 1.1	av. 1.8
	15	6.3	7.0	1.1	16	3.2	3.5
	30	12.5	13.7	1.1	17	3.4	3.7
C	45	17.4	19.3	1.1	17	3.4	3.7
	60	21.8	24.2	1.2	17	3.3	3.9
	90	27.9	31.3	1.0	17	3.5	3.5
				av. 1.1	av. 17	av. 3.4	av. 3.7

Reaction conditions:
A) 75°C, 1 *kg/cm²*, ST 0.0382 *mol/l*, $PdCl_2$ 0.00420 *mol/l*, MeOH 1.0 *mol/l*, Q 0.155 *mol/l*,
B) 75°C, 3 *kg/cm²*, ST 0.0796 *mol/l*, $PdCl_2$ 0.00353 *mol/l*, MeOH 1.0 *mol/l*, Q 0.155 *mol/l*,
C) 90°C, 3 *kg/cm²*, ST 0.0395 *mol/l*, $PdCl_2$ 0.00237 *mol/l*, MeOH 1.0 *mol/l*, Q 0.153 *mol/l*.
Values of k_{obs}, A_{obs}^{MC} and A_{obs}^{DS} were calculated by Eqs. (4), (7) and (8).

$$Z = \frac{R_{DS}}{R_{MC}} = \frac{A_{obs}^{DS}}{A_{obs}^{MC}} = \frac{[\mathrm{DS}]}{[\mathrm{MC}]}. \tag{6}$$

Then, the A_{obs}^{MC} and A_{obs}^{DS} can be expressed as

$$A_{obs}^{DS} = \frac{A_{obs}}{1+Z}, \tag{7}$$

$$A_{obs}^{MC} = \frac{A_{obs}}{1+Z}. \tag{8}$$

The separate calculations of A_{obs}^{MC} and A_{obs}^{DS} were made by these equations, in use of A_{obs} and Z_{obs} and the obtained values are listed in Table VII.

In the whole range of the examined pressure, effects of pressure on A_{obs}^{MC} and A_{obs}^{DS} were shown in Fig. 6. The solid curves show the theoretical ones calculated by the rate equation presented later. There were observed the pressures to bring about the maximum rates in both of MC formation and DS formation. For example, the maximum rate of DS formation was seen around at 12 *kg/cm²*, in case of reaction at 105°C.

The maximum rate of MC formation was attained at lower pressure than that at

Table VII. Observed values A^{MC} and A^{DS}

T (°C)	P_{co} (kg/cm^2)	$PdCl_2 \times 10^3$ (mol/l)	Z_{obs} (mole ratio)	$k_{obs} \times 10^5$ ($1/s$)	$A_{obs} \times 10^2$ ($l/mol \cdot s$)	$A^{MC}_{obs} \times 10^2$ ($l/mol \cdot s$)	$A^{DS}_{obs} \times 10^2$ ($l/mol \cdot s$)
75	1	4.20	0.6	9.1	2.2	1.4	0.81
	2	3.05	1.0	8.8	2.9	1.4	1.5
	3	3.53	1.7	10	2.8	1.1	1.8
	5	3.54	3.0	9.0	2.5	0.65	1.9
90	1	3.60	0.32	17	4.7	3.6	1.2
	3	2.37	1.1	17	7.2	3.4	3.7
	5	1.57	1.8	11	7.0	2.6	4.5
	10	1.38	3.6	7.7	5.6	1.2	4.4
105	2	5.81	0.42	9.1	16	11	4.7
	4	4.33	0.88	7.8	18	9.6	8.5
	9	7.01	2.0	13	19	5.9	12
	14	5.76	3.0	9.2	16	4.0	12

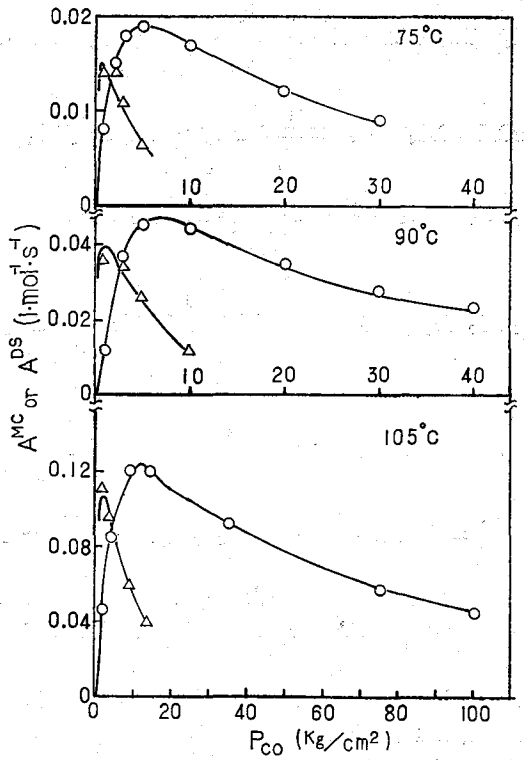


Fig. 6. Effect of carbon monoxide pressure on the rate
○ A^{DS}, △ A^{MC}
Solid lines: theoretical curves by Eq. (36) and Eq. (37)

the maximum rate of DS formation, and the pressure to give the maximum rate was shifted to the lower by increased temperature.

4. DISCUSSION

We proposed the following mechanism on the basis of our kinetic findings and also consulting with Stille's proposal as mentioned in introduction.

Mechanism:

$$PdCl_2+2L \xrightarrow{\text{fast}} \underset{\underline{1},\ C_1}{PdCl_2L_2}, \qquad L;\ PhCN\ (solvent) \tag{9}$$

$$PdCl_2L_2+CO \underset{}{\overset{K_1}{\rightleftharpoons}} \underset{\underline{2},\ C_2}{PdCl_2(CO)L}+L, \tag{10}$$

$$PdCl_2(CO)L+CO \overset{K_2}{\rightleftharpoons} \underset{\underline{3},\ C_3}{PdCl_2(CO)_2}+L, \tag{11}$$

$$PdCl_2(CO)L+PhCH=CH_2 \underset{k'_3}{\overset{k_3}{\rightleftharpoons}} \underset{\underline{4},\ C_4}{PdCl_2(CO)(PhCH=CH_2)}+L, \tag{12}$$

$$PdCl_2(PhCH=CH_2)(CO)+MeOH+L \underset{k'_4}{\overset{k_4}{\rightleftharpoons}} \underset{\underline{5},\ C_5}{PdCl(CO_2Me)(PhCH=CH_2)L}+HCl, \tag{13}$$

$$PdCl(CO_2Me)(PhCH=CH_2)L+L \underset{k'_5}{\overset{k_5}{\rightleftharpoons}} \underset{\underline{6},\ C_6}{Pd[CH(Ph)CH_2CO_2Me]ClL_2}, \tag{14}$$

$$PdCl[CH(Ph)CH_2CO_2Me]L_2 \xrightarrow{k_6} \underset{[MC]}{PhCH=CHCO_2Me}+HCl+2L+Pd, \tag{15}$$

$$PdCl[CH(Ph)CH_2CO_2Me]+CO \xrightarrow{k_7} \underset{\underline{7},\ C_7}{PdCl[\overset{O}{\overset{\|}{C}}CH(Ph)CH_2CO_2Me]L_2}, \tag{16}$$

$$PdCl[\overset{O}{\overset{\|}{C}}CH(Ph)CH_2CO_2Me]L_2+MeOH \xrightarrow{k_8} \underset{[DS]}{PhCH(CO_2Me)CH_2CO_2Me}+HCl+2L+Pd, \tag{17}$$

$$Pd+2HCl+O=\langle\rangle=O+2L \xrightarrow{\text{fast}} PdCl_2L_2+HO-\langle\rangle-OH, \tag{18}$$

where K_i's stand for equilibrium constants, k_i's for rate constats, the underlined figures for the respective compounds and C_i's for the concentrations of the respective compounds.

The depression of rate by excess pressure of carbon monoxide is the well known fact in the "Oxo" reaction, but this phenomenon has never been found in the palladium-catalyzed carbonylation reaction.

Lutton *et al.*[4] have reported the existence of $Pt(CO)Cl_2$ and $Pt(CO)_2Cl_2$, so we assumed the equilibrium formations of 2 as the reactive species and 3 as the inactive species in order to explain the pressure effect on the rate.

From the facts of no difference in the catalytic action between $PdCl_2$ and 1 and no dependence of the rate on benzoquinone concentration as mentioned previously, step (9) and (18) are to be fast.

No DS formation was occurred, when MC was used as the starting material for ST and the reaction was carried out for 2 h under the same conditions as in the selective formation of DS; MC 0.08 *mol/l*, $PdCl_2$ 0.0035 *mol/l*, MeOH 0.25 *mol/l*, Q 0.15 *mol/l*, 105°*C*, 150 *Kg/cm*^{2}.

According to this fact, we can reject the consecutive course of DS formation *via* the carbonylation of MC, and also neglect the reverse reaction in step (15). As no reverse reaction is generally considered in the carbonylations of alkyl or aryl platinum complex and palladium complex[5], we also omit the reverse reaction in step (16).

Assuming the rapid pre-equilibration for steps (10) and (11), K_1 and K_2 can be expressed as

$$K_1H=\frac{C_2}{C_1P_{co}}, \tag{19}$$

$$K_2H=\frac{C_3}{C_2P_{co}}, \tag{20}$$

where H denotes Henry's constant.

Applying the steady-state approximation to formations of 4, 5, 6 and 7, we have the following expressions:

$$R_4=k_3[\mathrm{ST}]C_2-(k_3'+k_4[\mathrm{MeOH}])C_4+k_4'C_5=0, \tag{21}$$

$$R_5=k_4[\mathrm{MeOH}]C_4-(k_4'+k_5)C_5+k_5'C_6=0, \tag{22}$$

$$R_6=k_5C_5-(k_5'+k_6+k_7HP_{co})C_6=0, \tag{23}$$

$$R_7=k_7HP_{co}C_6-k_8[\mathrm{MeOH}]C_7=0, \tag{24}$$

where $R_i=dC_i/dt$, $i=4, 5, 6, 7$.

In Eq. (21), k_3' is supposed to be negligibly small compared with $k_8[\mathrm{MeOH}]$, since the rate was not determined by MeOH concentration. Then, Eq. (21) can be written as

$$k_3[\mathrm{ST}]C_2-k_4[\mathrm{MeOH}]C_4+k_4'C_5=0. \tag{25}$$

From Eq. (24), C_6 is given as

$$C_6=\frac{k_8[\mathrm{MeOH}]}{k_7HP_{co}}C_7. \tag{26}$$

By the use of Eqs. (22), (23), (24), and (25), C_2 is given as

$$C_2=\frac{k_8[\mathrm{MeOH}](k_6+k_7HP_{co})}{k_3k_7HP_{co}[\mathrm{ST}]}. \tag{27}$$

Assuming the sum of C_1, C_2 and C_3 is much larger than that of C_4, C_5, C_6 and C_7, and using Eqs. (19) and (20), we have Eq. (28) with respect to the material balance of palladium.

$$[\mathrm{PdCl_2}]_0\fallingdotseq C_1+C_2+C_3=\frac{K_1K_2H^2P_{co}^2+K_1HP_{co}+1}{K_1HP_{co}}C_2. \tag{28}$$

The combination of Eqs. (27) and (28) leads to the following expression as to C_7.

$$C_7=\frac{K_1k_3k_7H^2P_{co}^2[\mathrm{ST}][\mathrm{PdCl_2}]_0}{k_8[\mathrm{MeOH}]\{K_1K_2k_7H^3P_{co}^3+(K_1k_7+K_1K_2k_6)H^2P_{co}^2+(K_1k_6+k_7)HP_{co}+k_6\}} \tag{29}$$

Finally, we get the rate equation of DS formation and that of MC formation as follows.

$$R_{DS}=\frac{(HP_{co})^2[\mathrm{ST}][\mathrm{PdCl_2}]_0}{B(HP_{co})^3+C(HP_{co})^2+DHP_{co}+E}, \tag{30}$$

$$R_{MC}=\left(\frac{k_6}{k_7}\right)\frac{HP_{co}[\mathrm{ST}][\mathrm{PdCl_2}]_0}{B(HP_{co})^3+C(HP_{oc})^2+DHP_{co}+E}, \tag{31}$$

where $B=K_2/k_3$, (32)

$C=(K_2k_6+k_7)/k_3k_7$, (33)

$D=(K_1k_6+k_7)/K_1k_3k_7$, (34)

$E=k_6/K_1k_3k_7$. (35)

Equations (30) and (31) are consistent with the experimental facts as to the concentration of ST and that of catalyst; the rate was found to be of the first order with respect to the respective concentrations of them.

Next, we made the examination as to whether Eqs. (30) and (31) were valid for the pressure effect.

Comparing the experimental equations of (2) and (3) with the derived rate equations of (30) and (31), we have expressions for A^{DS} and A^{MC} as

$$A^{DS}=\frac{(HP_{co})^2}{B(HP_{co})^3+C(HP_{co})^2+DHP_{co}+E}, \tag{36}$$

and

$$A^{MC}=\frac{HP_{co}}{B(HP_{co})^3+(HPC_{co})^2+DHP_{co}+E}. \tag{37}$$

Reciprocal of A^{DS} is written as

$$\frac{1}{A^{DS}}=BHP_{co}+C+\frac{D}{HP_{co}}+\frac{E}{(HP_{co})^2}. \tag{38}$$

According to Eq. (38), the linear relationship is to be expected between the reciprocal of A_{obs}^{DS} and the pressure of carbon monoxide if the third and the fourth term are small compared with the first and the second term. Plots of $1/A_{obs}^{DS}$ *vs.* P_{co} yielded straight lines at each given temperature and in the pressure range of suppressing rates, as seen in Fig. 7.

The values of B and C were obtained from slopes and intercepts respectively, as summarized in Table VIII.

Equation (38) can be rewritten as

$$\left(\frac{1}{A^{DS}}-BHP_{co}-C\right)P_{co}=\frac{D}{H}+\frac{E}{H^2P_{co}}. \tag{39}$$

The values of the left hand term calculated by the use of A_{obs}^{DS}, B and C, were plotted against $1/P_{co}$ in the lower pressure range of accelerating rates, and the linearity was proved to be valid between them as shown in Fig. 8. Values of D and E were calculated from the slope and the intercept of each straight line in Fig. 8 and obtained values are listed in Table VIII.

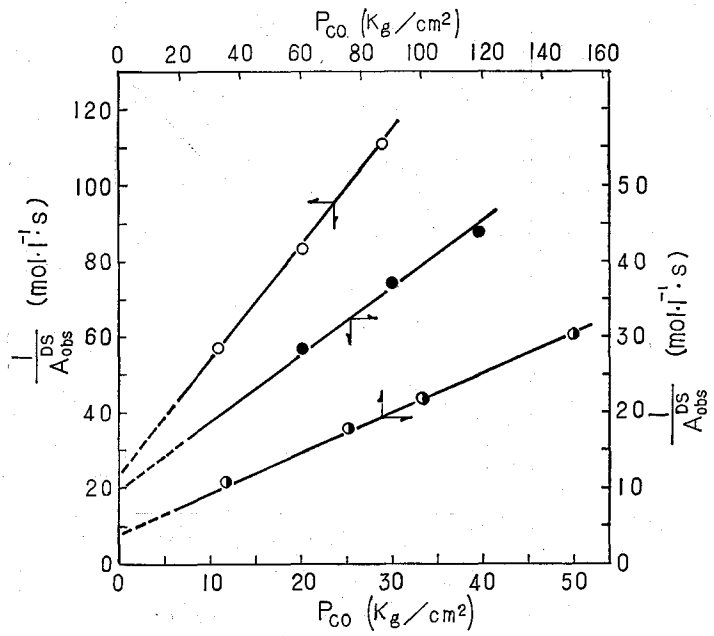


Fig. 7. Plot of $1/A^{DS}_{obs}$ *vs.* P_{CO}
○ 75°C, ● 90°C, ◑ 105°C

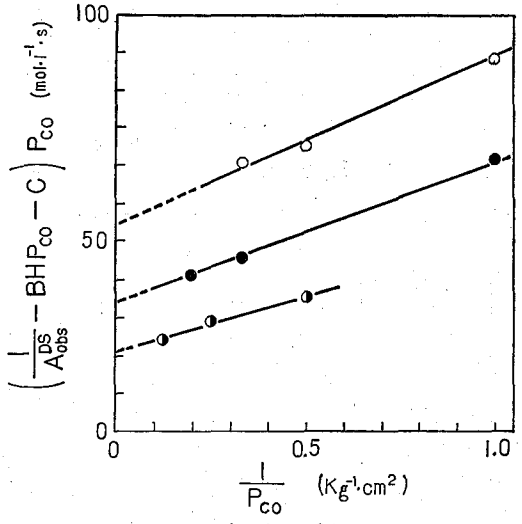


Fig. 8. Examination of Eq. (39)
○ 75°C, ● 90°C, ◑ 105°C

From Eqs. (30) and (31), we get expression for the mole ratio of produced DS to MC or the ratio of R_{DS} to R_{MC} as the following.

$$Z=\frac{R_{DS}}{R_{MC}}=\left(\frac{k_7H}{k_6}\right)P_{co} \tag{40}$$

The relationship between Z_{obs} and P_{co} are shown in Fig. 9, where Z_{obs}'s in Table

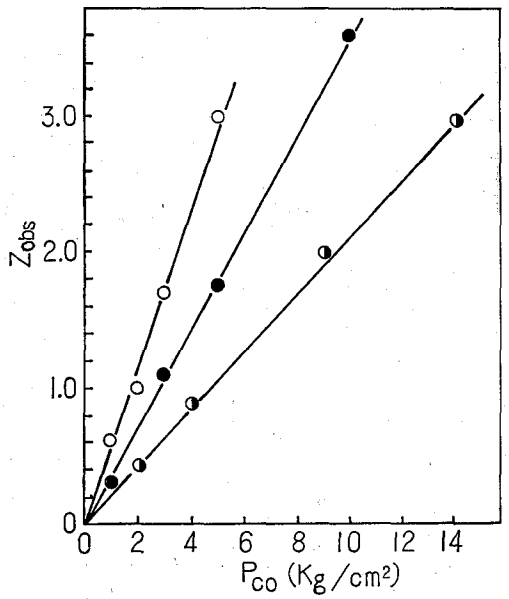


Fig. 9. Relationship between Z and P_{CO}

$$Z \equiv \frac{\text{produced DS } (mol)}{\text{produced MC } (mol)}$$

○ 75°C, ● 90°C, ◑ 105°C

VII were used.

Equation (40) was found to be content with the kinetic observations in the whole range of investigated pressures. The values of k_7/k_6, obtained from the tangent of each line at the given temperature, are listed in Table VIII. By the use of values of B, C, D and E, and Eqs. (32), (33), (34) and (35), values of K_1, K_2, k_3 and k_7/k_6 were obtained at each temperature, as listed in Table VIII.

Table VIII. Summary of constants in rate equations

Constants \ Temperature	75°C	90°C	105°C	Notes
$H\times10^2$ $(kg^{-1}cm^2)$	1.2	1.1	1.0	from Fig. 1
$B\times10^{-1}$ $(l\cdot mol^{-1}\cdot s)$	25	7.9	1.8	from Fig. 7
$C\times10^{-1}$ (s)	2.3	1.0	0.40	
$D\times10$ $(mol\cdot l^{-1}\cdot s)$	6.6	3.7	2.1	from Fig. 8
$E\times10^3$ $(mol^2\cdot l^{-2}\cdot s)$	6.3	4.6	3.0	
$k_7/k_6\times10^{-1}$ $(l\cdot mol^{-1})$	4.7	3.2	2.2	from Fig. 9
$K_1\times10^{-1}$ $(l\cdot mol^{-1})$	6.2	5.4	4.7	from the combination of Eqs. (32), (33) and (34)
$K_2\times10^{-1}$ $(l\cdot mol^{-1})$	1.5	1.1	0.61	
$k_3\times10^2$ (s^{-1})	5.7	14	32	
$K_1\times10^{-1}$ $(l\cdot mol^{-1})$	5.8	5.4	4.8	from the combination of Eqs. (32), (33) and (35)
$K_2\times10^{-1}$ $(l\cdot mol^{-1})$	1.5	1.1	0.57	
$k_3\times10^3$ (s^{-1})	5.8	13	31	

Temperature coefficients are -4.3 *kcal/mol*, -11.7 *kcal/mol*, 21 *kcal/mol* and -7 *kcal/mol* for K_1, K_2, k_3 and k_7/k_6, respectively.

Higher activation energy for k_6 than k_7 is consistent with the experimental fact of the temperature enhancement of β-H elimination in the intermediate 6 to result in the selective formation of MC.

Finally, the theoretical curves of A^{DS} and A^{MC} were calculated as the function of P_{co} by the use of Eqs. (36) and (37), and values of constants given in Table VIII. Theoretical curves thus obtained, reproduced the experimental values including the part of the peak, as shown in solid curves of Fig. 6.

As discussed thus far, the proposed mechanism and the derived rate equations have been found to give the quantitative explanation to the experimental results in the whole range of this kinetic study.

REFERENCES

(1) D. E. James, L. F. Hines, and J. K. Stille, *J. Amer. Chem. Soc.* **98**, 1810 (1976).
(2) D. W. Fenton and P. S. Steinwand, *J. Org. Chem.*, **37**, 2634 (1972).
(3) J. R. Doyle, *Inorg. Synth.*, **6**, 218 (1960).
(4) J. W. Lutton and P. W. Parry, *J. Amer. Chem. Soc.*, **76**, 4271 (1954).
(5) R. W. Glyde and R. J. Mawby, *J. Inorg. Chem.*, **10**, 854 (1971).
N. Sugita, J. V. W. Minkiewitz, and R. F. Heck, *ibid.*, **17**, 2809 (1978).